

kylation of β -keto esters. The fact that 19, 20, and 22 are readily available from the ketones 17 and 21 using a new conjunctive reagent 18¹¹ makes this 1,3 shift a lynchpin in a new cyclopentanone synthesis. The formation of 10, 11, and 12 illustrate applications of this new methodology in prostaglandin⁹ and steroid synthesis.

The mechanism of this 1,3 shift can be thought to involve an oxidative addition of the allyl ether to palladium(0) as in eq 2 to form a zwitterion 23.12 This intermediate collapses by



C alkylation to form the observed product. The regiochemistry of the collapse is quite interesting in that a five-membered-ring product is observed, even in the case of R' = H where sevenmembered-ring formation could have proceeded by attack at the less hindered carbon of the allyl unit.13 These results stand in stark contrast to cyclizations to form lactones in which the larger of the two possible ring sizes dominates even when an eight-membered ring results rather than a six.14 Applications and additional mechanistic studies into this metal-catalyzed 1,3 shift are underway.¹⁵ This new reaction illustrates an ability of a transition metal to change the normal rules of reactivity of an organic system.

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 This compound has been fully characterized by spectral means and ele-
- mental analysis and/or elemental composition by high resolution mass spectroscopy
- spectroscopy. Selected spectral data are as follows. **8**: IR (CHCl₃) 1700, 1640 cm⁻¹; NMR (270 MHz) δ 0.87 (t, J = 6 Hz, 3 H), 1.16–1.92 (m, 9 H), 2.27 (m, 1 H), 3.02 (m, 1 H), 3.29 (dddd, J = 18.5, 9, 4.5, 1.5 Hz, 1 H), 3.67 (s, 3 H), 3.77 (m, 1 H), 4.35 (d, J = 12 Hz, 1 H), 4.56 (two d, J = 12 Hz, 1 H), 4.86 (m, 1 H), 5.35 (br s, 1 H), 5.67 (m, 2 H), 7.30 (br s, 5 H); mol wt calcd for C₂₂H₃₀O₄ 358.2144, found 358.2144, 5: IR (CCl₄) 1700, 1635 cm⁻¹; NMR (CCl₄) δ 1.3–1.7 (m, 4 H), 1.62 (t, J = 1 Hz, 3 H), 1.7–2.1 (m, 6 H), 2.5–3.3 (m, 2 H), 3.51 (s, 3 H), 4.5 (br t, J = 7 Hz, 1 H), 5.55 (br m, 1 H), Anal. (C₁₄H₂₀O₃) C, H, mol wt. 6: IR (CCl₄) 1695, 15590, 1555 cm⁻⁷, NMR (270 MHz, CCl₄) δ 1.88–2.35 (m, 4 H), 2.81 (t, J = 8 Hz, 2 H), 3.05 (m, 1 H), 3.33 (dddd, J = 1.5, 8.7, 4.5, 1.5 Hz, 1 H), 3.68 (s, 3 H), 4.95 (t, J = 7.2 Hz, 1 H), 5.39 (t, J = 1.5 Hz, 1 H), 6.41 (br s, 1 H), 6.90 (d, J = 8 Hz, 1 H), 7.26 (m, 2 H). Anal. (C₁₇H₁₇BrO₃) C, H. 7: IR (CCl₄) 1700, 1638, 1595, 1485 cm⁻⁷; NMR (6) $\begin{array}{l} (I, J=1.5 \ \text{Hz}, 1.7), 0.5 \ \text{Hz}, 1.7), 0.5 \ \text{Hz}, 1.7), 1.2 \ \text{Hz}, 1.7),$

H), 3.70 (s, 3 H), 4.93 (t, J = 7.5 Hz, 1 H), 6.39 (s, 1 H), 6.90 (d, J = 7.7 Hz, 1 H), 7.27 (m, 2 H). Anal. (C₁₈H₁₉BrO₃) C, H, mol wt. **12:** IR (CHCl₃) 1755, 1725, 1655 cm⁻¹; NMR (270 MHz, CDCl₃) δ 0.87 (t, J = 6 Hz, 3 H), 1.16-1.79 (m, 8 H), 2.09 (m, 4 H), 3.02 and 3.00 (two d, J = 11 Hz, 1 H), 1.16–1.79 (iii, 8 H), 2.09 (iii, 4 H), 3.02 and 3.00 (iwo d, 5 \pm 1 H H, 3.70 (m, 1 H), 3.75 and 3.74 (iwo s, 3 H), 4.28–4.56 (m, 2 H), 5.50 (dd, J = 15, 7.5 Hz, 1 H), 5.63 (dd, J = 15, 6.7 Hz, 1 H), 7.31 (m, 5 H); mol wt calcd for C₂₂H₃₀O₄ 358.2144, found 358.2154. (*E*)-9: IR (CDCl₃); 1760, 1740 cm⁻¹; NMR (270 MHz, CDCl₃) δ 1.04 (s, 3 H), 1.45–2.47 (m, 9 H), 2.47–2.88 (m, 2 H), 3.27 (m, 1 H), 3.73 (s, 3 H), 5.50 (br s, 1 H); ¹³C MHz, CDCl₃) δ 1.38 (s, 3 H), 1.48–2.71 (m, 12 H), 3.61 (s, 3 H), 5.55 (m, 1 H); ¹³C NMR (C₂D₆) δ 20.5 (q), 22.7, 23.4, 23.9, 25.7, 28.9, 37.6, 51.2, 56.3, 59.8, 123.5, 135.7, 171.0, 214.0; mol wt found 236.1415. (*E*)-+ (*Z*)-11: IR (CCl₄) 1755, 1735, 1640, 1590, 1470 cm⁻¹; NMR (270 MHz, C₆D₆) 1.03 (s, 1 H, *E* isomer), 1.40 (s, 2 H, *Z* isomer), 1.5–2.40 (m, 9 H), 20.9 (c, 2 H) 2.00 (b, 2 0 H); 22.2 H) 6.0 (b, 2 C) (b, 7.15 (fit, 1 H); -C NWH (c₆D₆) o 14 (4), 20 (4), 24, 27, 27, 26, 37, 35, 55, 56, 60, 121, 123, 124, 128, 131, 133, 137, 140, 170, 204, 208, 213; mol wt calcd for C₁₈H₁₉⁷⁹BrO₃ 362,0518, found 362,0516. (*E*) + (*Z*)-10: IR (CDCl₃) 1765, 1725, 1655, 1590, 1480 cm⁻¹; NMR (270 MHz, CDCl₃) δ 1.7–1.9 (m, 1 H), 2.3–2.6 (m, 5 H), 2.80 (t, *J* = 8 Hz, 2 H), 3.26 (d, *J* = 11.5 Hz, 1 H), 3.39 (td, *J* = 11.5, 6.2 Hz, 1 H), 3.69 (s, 0.21 H), 3.76 (s, 2.79 H), 6.4 (m, 0.21 H), 6.20 (tz, 0.02 H) 6.80 (d, *J* = 7.5 Hz, 1 H), 3.75 (td, *J* = 6.00 (tz, 0.02 H) 6.80 (d, *J* = 7.5 Hz, 1 H), 3.76 (s, 2.79 H), 6.4 (tz, 0.02 H) 6.80 (tz, 0.21 H), 6.20 (tz, 0.21 H) 6.80 (tz, 0.21 H), 6.20 (tz, 0.21 H), 6.80 (tz, 0.21 H), 6.20 (tz, 0.21 H), 6.80 (tz, 0.21 H), 6.80 (tz, 0.21 H), 7.75 6.14 (br s, 0.07 H), 6.28 (br s, 0.93 H), 6.88 (d, $J=7.5\,\text{Hz},$ 1 H), 7.25 (m, 2 H); ^{13}C NMR (C_6D_6) δ 25, 26, 28, 38, 48, 52, 59, 120, 122, 127.5, 130 133, 137, 141, 169, 209. Anal. $(C_{17}H_{17}BrO_3)$: C, H, Br, mol wt. (7) This catalyst was prepared in an analogous manner to the preparation of

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A New Diene Synthesis via Organopalladium Chemistry

Sir:

Approaches to dienes via carbonyl olefination procedures usually lead to stereoisomeric mixtures. We report here that a new palladium catalyzed decarboxylative elimination of the adducts from enals and carboxylate enolates, a prototype for transition metal catalyzed fragmentation reactions, can lead to a highly stereocontrolled diene synthesis from erythro-threo mixtures as outlined in eq 1. This new fragmentation reaction

has also generated a cyclohexadiene synthesis in conjunction with Diels-Alder reactions. Application of this method to a synthesis of the insect sex pheromones bombykol1 and codlemone² is also reported. We believe that this study represents the first case of activation of a substrate for loss of CO_2 by palladium catalysts.

Reported methods³⁻⁵ that effect the elimination of β -hydroxycarboxylic acids to olefins do so with high stereospecificity⁸—a fact which necessitates stereodefined syntheses of the β -hydroxy compounds in order to translate into a stereodefined olefin synthesis.³⁻⁸ Unfortunately, the most direct approach of adding the enolate of a carboxylic acid⁹ to a carbonyl group produces a diastereomeric mixture, frequently in a 1:1 ratio. Here a stereoselective⁸ diene synthesis where both stereoisomeric adducts can lead to the same diene is required. Addition of the dianion from propionic acid to (*E*)-2-phenylcrotonaldehyde and from phenylacetic acid to (*E*)-cinnamaldehyde followed by in situ acetylation with acetyl chloride led to precursors **1** and **2** as 1:1 and 3:1 diastereomeric mixtures in 84 and 92%, respectively. Subjection of **1** or **2** to 3-5 mol %

$$R^{1} \xrightarrow{R^{2}}_{OAc} \xrightarrow{CO_{2}H}_{(C_{2}H_{5})_{3}N} R^{1} \xrightarrow{R^{2}}_{(C_{2}H_{5})_{3}N} R^{1} \xrightarrow{R^{2}}_{R^{1}} R^{1}$$

$$\frac{1}{2} \qquad R^{1} = CH_{3}, R^{2} = Ph \qquad 4$$

$$\frac{1}{2} \qquad R^{1} = Ph \qquad R^{2} = H \qquad 5$$

of tetrakis(triphenylphosphine)palladium (3) and 1.1 equiv of triethylamine in refluxing THF or, preferably, in toluene at 85 °C produced the E,E dienes 4 and 5 in 61-84 and 76-89% yields. In subsequent studies, use of Me₂SO as solvent further facilitates the reaction. For 4, the E, E configuration is confirmed by the 15-Hz coupling constant for the newly introduced double bond, the quantitative formation of the Diels-Alder adduct with N-phenylmaleimide at room temperature to form an adduct identical with an authentic sample, and comparison with an authentic sample.¹⁰ The high stereoselectivity of this diene synthesis was further verified by subjecting each diastereomer of 1 separately to the reaction conditions. For 5, identification was confirmed by comparison with an authentic sample spectroscopically and by mixture melting point (151-153 °C).¹¹ Previously, diene 4 was only available as an isomeric mixture by the Wittig reaction in studies directed toward streptonigrin by Weinreb.¹⁰

The stereochemistry of the double bond originally present in the precursor remains unaffected as illustrated in the synthesis of the insect sex pheromones codlemone $(8)^{12}$ and bombykol (11).^{13,14} In the former case, reaction of 6 (diastereomeric ratio 1.3:1) with 3 mol % of catalyst at room temperature, 85 °C in PhCH₃, or reflux in THF led to 7 in 77–82%



yield containing 22% Z, E isomer. Hydrolysis (CH₃OH, H₂O, TsOH, 60 °C) produced **8.** NMR and VPC confirmed the presence of two compounds (78:22, E, E/Z, E) with the 10,11 double bond being E in both.¹⁵ Crystallization from pentane produced pure codlemone (**8**), mp 27.5–28.5 °C (lit.¹² mp 28 °C), whose spectral properties agree with those reported.

Precursor 9 when subjected to the same conditions produced 10 contaminated by $\sim 10\% Z_z Z$ isomer. Hydrolysis, as above, gave pure bombykol (11) after TLC separation whose properties agree with those reported.¹³ NMR analysis at 270 MHz confirmed the Z,E stereochemistry as well: δ 5.29 (dt, J = 10.8, 7.5 Hz), 5.64 (dt, J = 15.0, 7.5 Hz), 5.94 (ddt, J = 10.8, 10.8, 1.5 Hz), 6.30 (ddt, J = 15.0, 10.8, 1.5 Hz).

The fact that the Z, E isomer forms in the latter case as well as the fact that the stereochemistry of the diene is independent of reaction time and shows no detectable variation with reaction temperature indicates the stereochemistry observed is kinetically controlled. In each case, a high to exclusive preference for introducing an E double bond is observed. A scheme to account for these observations is presented in eq 2. Such a



scheme does not preclude interconversion among the isomers by any mechanism, but suggests that the relative rates of disengagement of CO₂ controls the stereochemistry of the diene.¹⁶ To confirm that both anti (path a) and syn (path b) fragmentation pathways are possible, both isomers of **12** were subjected to **3** to give **13**^{17,19d} in 75–85% yield. Such an inter-



pretation assumes formation of the π -allyl complex and its subsequent fragmentation is faster than stereochemical isomerization of starting material.^{16b}

This last result also illustrates the use of this approach as a cyclohexadiene synthesis via Diels-Alder reactions. This approach was generalized as shown by the syntheses of dienes **14–18**.^{17,18} Special note should be taken of the synthesis of **17** in which a dienolacetate is produced (thus heteroatom substitution on the diene is tolerated) and of **18** in which a 1,3 substitution pattern emerges from a cycloaddition sequence. An alternative cyclohexadiene synthesis with a similar substitution pattern is illustrated by the conversion of **19** into **20**²³ (71% yield). The precursor **19** stemmed from hexanal and methyl acetoacetate by condensation-decarboxylation,²⁰ reduction,²¹ and acetylation.²¹ Under these conditions aromatization has not been observed. Control of reaction time may

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be necessary. For example, in the production of 15, a reaction time of \sim 4 h sufficed; increasing the time to 18 h led to clean isomerization to methyl cyclohexa-1,4-diene-1-carboxylate^{17,19e} which was isolated in 64% yield. Such an observation may be general.



diene	R	R [†]	R ²	X	%
14	Н	Н	н	н	87
15 ^{19a}	н	н	CO_2CH_3	Н	71
16 ^{19b}	н	C_2H_5	H	Н	69
17 ^{19c}	н	Ъ	н	OAc	81
1817,23	CH ₃	н	Ph	Н	77
19 ^{19b}	н	н	C ₂ H ₅	н	69



Thus, this stereocontrolled diene synthesis represents a prototype fragmentation reaction catalyzed by palladium. It is interesting to note that loss of CO₂ to form diene is faster than loss of a proton to form a dienecarboxylic acid. Thus, this reaction complements the previous diene synthesis.²² We attribute the high to exclusive stereocontrol observed to the complexation of the allyl cation by palladium in the intermediate which increases its lifetime and thus allows ejection of CO₂ in both a syn and anti fashion. Steric interactions presumably are responsible for formation of the E olefin. Thus, reactions in which the stereochemistry of the substrates determines the stereochemistry of the products is not always desirable. The present study illustrates one such case. The possibility that other fragmentation reactions may be initiated by palladium, or other transition metals, with benefits of the type reported here are under active investigation.

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Electron Affinity of HO₂ and HO_x Radicals¹

Sir:

The HO₂ radical is of great importance in flames, in oxidation at both low and high temperatures, in biological systems, and in the chemistry of the atmosphere (stratosphere and troposphere).^{2a} The anion of the radical HO₂⁻ appears very important in solution oxidations^{2a} and in the aqueous chemistry of O₃. A related species HO_3^- appears to be very important in the chemistry of O_3 reactions with saturated species at temperatures below 0 °C.^{2b} A recent review³ lists a value for the electron affinity of HO2. [EA(HO2.)] of 4.6 eV. This value comes from a necessarily crude estimate made over 40 years ago. It appears to be much too high to be plausible.

There is a considerable amount of fairly reliable data available on the aqueous thermochemistry of H_2O_2 and $HO_2^{-4,5}$ as well as on the related species HO_2 (aqueous) and